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(54) MULTI-LAYER BIODEGRADABLE PLASTIC FILM

(57)Abstract:

PURPOSE: To improve heat properties by setting the melting temperature for a biodegradable plastic film forming the outermost layer lower by at least specified temperature than the melting temperature of a film composed of a polylactic polymer or a composition having polylactic polymer as its main component.

CONSTITUTION: A multi-layer biodegradable plastic film comprises a film composed of a polylactic polymer or a composition having the same as main component, and at least one outermost layer of a biodegradable plastic film, and the melting temperature T_m for the biodegradable plastic film forming the outermost layer is lower by at least 10°C than the m.p. T_m for the film comprising the polylactic copolymer or the composition having the same as main component. The polylactic polymer to be used is a copolymer of polylactic acid or lactic acid and other hydroxycarboxylic acid, or a composition thereof, and other polymeric materials may be mixed in the range not inhibiting the effect.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to multilayer biodegradability plastic film excellent in heat-sealing nature.

[0002]

[A Prior art and Object of the Invention] The general packing-material application which made the snack confectionery bag the typical example is begun, and the film which was excellent in broad applications, such as agricultural materials, construction materials, and biomedical materials, at heat-sealing nature is demanded.

[0003] In case the so-called "heat sealing" of the film excellent in heat-sealing nature which sticks a film comrade by heat and the pressure, or is pasted up using a heating bar, a hot plate or a heating roller, etc. is carried out, it points to a film with the wide temperature requirement obtained by being stabilized in the bond strength for which it asks. That is, the film excellent in heat-sealing nature can obtain various kinds of film processing products simple by heat sealing.

[0004] Since the film base material is hard when less than the above-mentioned temperature requirement in the case of heat sealing, sufficient bond strength is not obtained, but bond strength falls owing to them at the same time a film base material will become soft too much, a pinhole or a wrinkling will arise and it will cause degradation of an appearance, if it exceeds.

[0005] Moreover, if heat-sealing nature is scarce, the various problems that must do a heat-sealing activity in a narrow temperature requirement, high temperature control capacity is searched for, and equipment becomes expensive and that fatigue of an operator's mind and body with a high percent defective with bad productivity is intense will occur.

[0006] Then, there are not few cases where the film which improved heat-sealing nature is used, by using the raw material of a special polymer design for the application which carries out the need of the heat sealing with general-purpose films, such as polyolefine, and PET (polyethylene terephthalate), PVC (polyvinyl chloride), or performing a blend and laminating of a different-species raw material.

[0007] On the other hand, when it is rejected from the rise about an environmental problem in natural environment to a plastic working article at large in recent years, the plastic which does not have a bad influence on the natural environment which decomposes and disappears with time is called for.

[0008] However, the conventional plastic film product was stable over the long period of time in natural environment, and moreover, since relative bulk density was small, the trouble of having promoted the ephemerization of a trash reclaimed ground or spoiling a natural scene and the living environment of wildness animals and plants was pointed out.

[0009] Then, biodegradability plastic material attracts attention today. Biodegradable plastics are the inside of soil, and underwater, collapse and decomposition advance gradually according to hydrolysis or biodegradation, and becoming a harmless decomposition product according to an operation of a microorganism finally is known.

[0010] The biodegradable plastic by which current and utilization are considered is divided roughly into

aliphatic series polyester, Denaturation PVA (polyvinyl alcohol), a cellulose ester compound, starch modification objects, and these blend objects.

[0011] As aliphatic series polyester, as a microorganism production system polymer, Pori (hydroxybutyric acid/valeric acid) is known as a synthetic system polymer, and the polylactic acid system polymer is known, respectively as the poly caprolactone, aliphatic series dicarboxylic acid, the condensation product of aliphatic series diol, and a semisynthesis system polymer, for example.

[0012] Although these biodegradable plastics have the description of a proper respectively and the application expansion according to it can be considered, since transparency, rigidity, thermal resistance, workability, etc. are outstanding as compared with other biodegradable plastics, as for a polylactic acid system polymer, expansion to the hard bright film application for which hard [PVC or PET] has been used conventionally is going to be achieved especially.

[0013] Especially the biaxial-stretching heat setting film that used the polylactic acid system polymer has a general-purpose film, an EQC, or the machine physical properties to surpass, since it is perfect biodegradability, a general packing material is begun and application is expected from the broad application.

[0014] However, the film made from the polylactic acid system polymer was lacking in heat-sealing nature, and when using it for various fields, such as a film processing product, it had become a practical big problem. Then, the purpose of this invention offers biodegradability plastic film excellent in heat-sealing nature.

[0015]

[Means for Solving the Problem] The melting out temperature T_m of the biodegradability plastic film which the summary of this invention has the film which consists of a constituent which makes a principal component a polylactic acid system polymer or this, and is multilayer biodegradability plastic film one [at least] outermost layer of whose is biodegradability plastic film, and forms said outermost layer is multilayer biodegradability plastic film characterized by being lower than the melting out temperature T_m of the film which consists of a constituent which makes a principal component said polylactic acid system polymer or this 10 degrees C or more. The biodegradability plastic film which the summary of different this invention has the film which consists of a constituent which makes a principal component a polylactic acid system polymer or this, and it is multilayer biodegradability plastic film one [at least] outermost layer of whose is biodegradability plastic film, and the film which consists of a constituent which makes a principal component said polylactic acid system polymer or this has a melting out temperature T_m , and forms said outermost layer is multilayer biodegradability plastic film characterized by being an amorphous film. It is desirable that the melting out temperature T_m of the film which consists of a constituent which makes a principal component said polylactic acid system polymer or this is 100 degrees C or more.

[0016] The polylactic acid system polymers used for this invention are the copolymers of polylactic acid or a lactic acid, and other hydroxycarboxylic acid, or these constituents, and other polymeric materials may be mixed in the range which does not check the effectiveness of this invention. Moreover, it is also possible to add additives, such as a plasticizer, lubricant, an inorganic filler, and an ultraviolet ray absorbent, and a modifier in order to adjust the physical properties and workability of a film.

[0017] L-lactic acid and D-lactic acid are mentioned as a lactic acid, and a glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, a 3-hydroxy valeric acid, a 4-hydroxy valeric acid, a 6-hydroxy caproic acid, etc. are typically mentioned as hydroxycarboxylic acid.

[0018] The polymerization method is possible also for adopting well-known approaches, such as a condensation-polymerization method and a ring-opening-polymerization method, and may use a small amount of chain elongation agent, for example, a diisocyanate compound, a diepoxy compound, an acid anhydride, acid chloride, etc. for the purpose of molecular-weight increase further. If the range of 60,000 to 1000 and 000 is desirable and turns around this range the bottom as weight average molecular weight of a polymer, practical use physical properties will produce a hardly discovered problem. Moreover, in turning a top, melt viscosity becomes high too much and is inferior to fabrication nature.

[0019] It is important that the melting out temperature T_m of the film (henceforth [it omits and] a

polylactic acid system film) which consists of a constituent which makes a principal component a polylactic acid system polymer or this here is 100 degrees C or more. Thermal resistance falls at less than 100 degrees C, and T_m causes a wrinkling etc. and is not practical in fabricating etc. Moreover, T_m of a Pori L-lactic acid gay polymer is 195 degrees C, and T_m falls as copolymerization components, such as D-lactic acid, a glycolic acid, and a 6-hydroxy caproic acid, increase. For this reason, in practice, $T_m(s)$ of the polylactic acid system film used for this invention are 100 degrees C or more and 195 degrees C or less.

[0020] Moreover, if crystalline polymers, such as a polylactic acid system polymer, increase the copolymerization ratio, the crystallization temperature T_c at the time of a temperature up rises, and the melting out temperature T_m tends to fall. At the temperature used as $T_c > T_m$, T_m is no longer observed substantially. That is, although it can disappear before T_m has fallen to 100 degrees C depending on selection of a copolymerization monomer, in this invention, a polylactic acid system film needs to have T_m .

[0021] The biodegradability plastic film by which a laminating is carried out to the polylactic acid system film mentioned above is biodegradability plastic film lower 10 degrees C or more than the melting out temperature T_m of the polylactic acid system film used, or biodegradability plastic film which is amorphism nature. As biodegradability plastic film, aliphatic series polyester other than polylactic acid and polylactic acid, Denaturation PVA, a cellulose ester compound, etc. can be used.

[0022] When a polylactic acid system film is used, it means that the polylactic acid system film was multilayered as biodegradability plastic film by which a laminating is carried out to a polylactic acid system film (base material).

[0023] As mentioned above, by adding copolymerization components, such as D or L-lactic acid, a glycolic acid, and a 6-hydroxy caproic acid, to a gay polymer, the polylactic acid system film with a melting out temperature T_m lower 10 degrees C or more than the polylactic acid system film used as a base material for which it asks can reduce a melting out temperature T_m , and can be obtained. As a film by which a laminating is carried out, since the melting out temperature T_m of a gay polymer is 195 degrees C, a polylactic acid system film 185 degrees C or less is used. Moreover, what is necessary is just to increase the copolymerization ratio further, in order to obtain the polylactic acid system film which is amorphism nature.

[0024] Aliphatic series polyester other than polylactic acid used as biodegradability plastic film by which a laminating is carried out by this invention cannot have alkylene and an ester bond as a basic frame, and can also introduce a urethane bond, amide association, ether linkage, etc. in the range which does not have real effect on biodegradability. Especially, using an isocyanate compound, a urethane bond can be introduced into a principal chain and molecular weight can be jumped up.

[0025] Specifically, the polymer obtained by condensing aliphatic series diol and aliphatic series dicarboxylic acid first is mentioned. As aliphatic series diol, ethylene glycol, 1,4-butanediol and 1, and 4-cyclohexane dimethanol etc. is mentioned, and a succinic acid, an adipic acid, a suberic acid, a sebacic acid, dodecane diacid, etc. are typically raised as aliphatic series dicarboxylic acid. After choosing one or more kinds from these, respectively and carrying out a condensation polymerization, the polymer which jumped up weight average molecular weight or more to 50,000 with the isocyanate compound if needed can have the usually same radical genuine article nature as 60-110-degree C T_m and polyethylene, and can use it for this invention preferably.

[0026] Moreover, a series of aliphatic series polyester which carried out ring opening polymerization of the annular lactone using the organic metal catalyst is mentioned. As a monomer, epsilon-caprolactone, delta-valerolactone, a beta-methyl-delta-valerolactone, beta propiolactone, PIBARO lactone, beta-butyrolactone, gamma-butyrolactone, etc. are mentioned typically, and a lactide and glycolide are mentioned further. Conditions are adjusted and a polymerization is carried out so that one or more kinds may be chosen from these and weight average molecular weight may become 30,000 or more. Although control of T_m is performed by selection of a monomer, it is usually 50-170 degrees C.

[0027] As other synthetic system aliphatic series polyester, a radical polymerization object with the 2-methylene -1 which is an annular ketene acetal, 3-dioxolane and 2-methylene -1, and 3-dioxepane etc. is

mentioned. [the polymer of a cyclic anhydride, oxiranes for example, a succinic anhydride and ethyleneoxide, propione oxide, or allyl glycidyl ether, ethylene,]

[0028] Moreover, the aliphatic series polyester a biosynthesis is carried out [polyester] by acetyl-coenzyme A (acetyl CoA) within fungus bodies including *Alcaligenes YUTOROFASU* is known. Although this aliphatic series polyester is mainly poly-beta-hydroxybutyric acid (Pori 3HB), in order to put the practical use property as plastics on **, it is industrially advantageous to devise a fermentation process, to usually copolymerize a valeric-acid unit (HV), and to make it the copolymer of Pori (3 HB-co-3HV). Generally HV copolymerization ratio is 0 - 40%, and Tm is 130-165 degrees C in this range. 4HB may be copolymerized instead of HV, or long-chain hydroxy alkanoate may be copolymerized. [0029] In the existing petroleum origin composition system polymer, although the polyvinyl alcohol (PVA) used as biodegradability plastic film by which a laminating is carried out by this invention is comparatively excellent in biodegradability, a PVA homopolymer has the too large cohesive force of a molecule, and since melting extrusion molding cannot be performed without the melting point, when film-izing, it receives the constraint on fabrication. Then, ethylene can be copolymerized or the vinyl acetate unit which usually disappears at a saponification process can be made to be able to remain, and it can reform and use so that it may have about 50-150-degree C Tm. The constituent which distributed starch etc. based on such a PVA system polymer in order to raise biodegradability has obtained evaluation fixed as biodegradability plastic material, and is called Denaturation PVA.

[0030] The cellulose ester compound used as biodegradability plastic film by which a laminating is carried out by this invention is a compound which usually acetic-ester-ized the hydroxyl group of a cellulose, and whenever [permutation] is between 2-3. A cellulose ester compound does not have Tm substantially. A plasticizer may be added in order to give melting fabrication nature. A plasticizer also has the work which adjusts Tg (glass transition temperature) of an ingredient. As a plasticizer, aliphatic series ester, fats and oils, for example, a dibutyl horse mackerel bait, dioctyl adipate, glycerol acetate, soybean oil, castor oil, linseed oil, etc. are preferably mentioned in consideration of biodegradability.

[0031] It is the purpose which adjusts the physical properties and workability of a film also to the biodegradability plastic film by which a laminating is carried out to a polylactic acid system film in the range which does not check the effectiveness of this invention, and it is also possible to add additives, such as a plasticizer, lubricant, an inorganic filler, and an ultraviolet ray absorbent, a modifier, or other polymeric materials.

[0032] The lamination of the multilayer biodegradability plastic film of this invention will not be limited especially if one [which uses a polylactic acid system film as a base material, and forms the outermost layer / at least] film is biodegradability plastic film, but in order to give double-sided heat-sealing nature and curl-proof nature, it can be used as the laminated film of the two-sort 3 lamination which made the inner layer the polylactic acid system film excellent in the mechanical characteristic, and used both outer layers as other biodegradability plastic film.

[0033] Moreover, it does not matter as a multilayer configuration of three or more layers in order to give other functionality, such as gas barrier property and steam barrier property. Moreover, you may make it the lamination for un-[vertical] from a main layer for [for low-pricing] an application with more desirable having curl nature.

[0034] As an approach of carrying out the laminating of the biodegradability plastic film to a polylactic acid system film, the approach used for usual is employable. For example, an approach etc. is mentioned typically sticking a film comrade using the approach of connecting two or more extruders with one mouthpiece, and carrying out the so-called co-extrusion, the approach of coating the ingredient of another kind on a kind of film which it began to roll, the approach of carrying out thermocompression bonding of two or more sorts of films in optimal temperature with a roll, a press machine, etc., or adhesives.

[0035] As the so-called dry lamination or adhesives in the case of carrying out wet lamination, although a vinyl system, acrylic, a polyamide system, a polyester system, a rubber system, an urethane system, etc. are generally used, when also making adhesives into biodegradability, protein, such as polysaccharide, such as starch, an amylose, and an amylopectin, and glia, gelatin, casein, a zein, a

collagen, polypeptides, unvulcanized natural rubber, or aliphatic series polyester is adopted preferably. [0036] In order for a polylactic acid system polymer to improve sharply the brittleness which it has essentially and to raise film reinforcement more, it is desirable to adjust planar orientation degree ΔP of the polylactic acid system film used as a base material to 3.0×10^{-3} to 30×10^{-3} .

[0037] ΔP expresses the amount of preferred orientation of the direction of a field to the thickness direction of a film, usually measures the refractive index of rectangular cross 3 shaft orientations, and is computed by the following formulas.

$$\Delta P = \{(\gamma + \beta) / 2\} - \alpha \quad (\alpha < \beta < \gamma)$$

Here, γ and β of a refractive index [parallel to a film plane] biaxial [rectangular] and α are the refractive indexes of the film thickness direction.

[0038] Although ΔP is dependent also on degree of crystallinity or crystal orientation, it is greatly dependent on the molecular orientation in a film plane. That is, or more [this invention prescribes ΔP which is 1.0×10 to three or less] three [3.0×10 to], it can be made to increase with a non-orientation sheet film by increasing molecular orientation in a film plane to 1 or the 2-way of a direction which intersects perpendicularly especially with the flow direction of a film and/or it.

[0039] In addition to all the known film extending methods, as an approach of increasing ΔP , the molecular orientation method using electric field or a magnetic field is also employable.

[0040] Usually, after quenching the sheet-like object or cylindrical object which carried out melting extrusion from the T die, I die, the round-head die, etc. by the cooling cast roll, water, a compressed air, etc. and making it solidify in the near condition amorphously, the approach of extending on one shaft or two shafts by the rolling method, the tenter method, tubular **, etc. is adopted desirably industrially.

[0041] What is necessary is for what is necessary to be just to use the polylactic acid system film by which extension processing was beforehand carried out when manufacturing the extended multilayer biodegradability plastic film and multilayering by a lamination, the so-called dry lamination, or wet lamination, and just to extend the extruded multilayer film on suitable conditions, when co-extruding.

[0042] Although the amount of ΔP is general, since this proper range changes with the presentation of a polymer, and heat histories of a non-extended sheet a part for extension temperature [of 50-100 degrees C], 5 times [1.5 times to] as many draw magnification [as this], and 100%/of extension rates -, and 10,000% as extension conditions at the time of paying one's attention only to a polylactic acid system film, it is decided suitably, looking at the value of ΔP .

[0043] In this way, the brittleness which it has essentially is improved sharply and mechanical strength of the polylactic acid system film extended is improving. It is the film of heat shrink nature and application expansion is possible on a shrink package, a contraction union package, or a contraction label.

[0044] However, it cannot use for many applications as which heat dimensional stability is required in the multilayer biodegradability plastic film for which ΔP mentioned above used the polylactic acid system film of 3.0×10^{-3} to 30×10^{-3} . So, in order to give heat dimensional stability to a polylactic acid system film, 20 or more J/g and $\{(\Delta H_m - \Delta H_c) / \Delta H_m\}$ are controlled for the difference ($\Delta H_m - \Delta H_c$) of amount of crystal heat of fusions ΔH_m when carrying out the temperature up of the film, and amount of heat of crystallization ΔH_c generated by crystallization in a temperature up or more to 0.75.

[0045] That is, when less than these conditions, the heat dimensional stability of a film is poor, it is easy to produce the secondary elaboration process warmed [aging / lamination, desiccation,] and the problem contracted during storage of summer, and practical use is not presented. If it exceeds these conditions, heat dimensional stability will become good and trouble will be lost practically.

[0046] ΔH_m and ΔH_c are calculated by the differential scanning calorimetry (DSC) of a film sample, and ΔH_m is a heating value required to dissolve all the crystals when carrying out a temperature up by part for programming-rate/of 10 degrees C, and is calculated from the area of the endoergic peak by the crystal fusion which appears near the crystalline melting point of a polymer. Moreover, ΔH_c is calculated from the area of the exothermic peak generated in the case of crystallization produced in a temperature up process.

[0047] deltaHm mainly takes a big value with a polymer with large crystallinity depending on the crystallinity of the polymer itself. In the perfect homopolymer of the L-lactic acid which incidentally does not have a copolymer, or D-lactic acid, it is 60 or more J/g, and deltaHm changes with the presentation ratios in the copolymer of these two sorts of lactic acids. deltaHc is an index related to the degree of crystallinity of that film when receiving the crystallinity of a polymer, and when deltaHc is large, crystallization of a film advances in a temperature up process. That is, it expresses that the degree of crystallinity of a film was relatively low on the basis of the crystallinity which a polymer has. On the contrary, when deltaHc is small, it expresses that the degree of crystallinity of a film was relatively high on the basis of the crystallinity which a polymer has.

[0048] That is, the one direction of [for increasing (delta Hm-delta Hc)] is that crystallinity builds the comparatively high film of degree of crystallinity for a high polymer in a raw material. In order for the degree of crystallinity of a film to make deltaHm of the polymer itself 20 or more J/g depending on the presentation of a polymer not a little, in the case which makes a copolymer from L-lactic acid and D-lactic acid, it is confirmed on the experiment that it is necessary to prepare the presentation ratio within the limits of 100:0-94:6 or within the limits of 0:100-6:94. Moreover, in order to reduce deltaHc (i.e., in order to raise the degree of crystallinity of a film), it is necessary to select the fabrication conditions of a film.

[0049] In order to raise the degree of crystallinity of a film in the fabrication process, especially tenter method biaxial extension, it is useful to gather draw magnification and to promote orientation crystallization, to heat-treat in the ambient atmosphere beyond crystallization temperature after extension, etc. In addition, heat dimensional stability can be given by heat-treating 3 seconds or more in 90 degrees C - 170 degrees C suitably above at least 70 degrees C, as a result of there having been an inclination for crystallization temperature to fall, and inquiring wholeheartedly when it is this invention so that deltaP was large. Heat dimensional stability improves, so that heat treatment time amount is so long that heat treatment temperature is high within the limits of this.

[0050]

[Example] Although an example is shown below, it is not limited to this invention by these.

[0051] (Example 1 of an experiment) the melt from 50mmphi monopodium extruder becomes a inner layer, and the melt from 30mmphi monopodium extruder becomes both outer layers -- as -- a two-sort three-layer T die -- it co-extruded using the mouthpiece. The thickness ratio of an outer layer / inner layer / outer layer was adjusted so that it might be set to 1/8/1, and on the whole, the 250-micrometer non-extended sheet was quenched after extrusion, and was extracted.

[0052] As a inner layer (base material), the polylactic acid (Lacty by Shimadzu Corp.) (Tm=170 degree C) of L body / D object =98/2, and weight average molecular weight 200,000 Bionolle 1010 (Tm=114 degree C) by Showa High Polymer Co., Ltd. which is aliphatic series polyester as an outer layer, the plaque cel H-7 (Tm=60 degree C) by Daicel Chemical Industries, Ltd., and Zeneka Make -- biotechnology pole D300G (Tm=162 degree C) -- and -- said -- D400G (Tm=153 degree C) were used. Moreover, similarly, polylactic acid was extruded by 30mmphi monopodium extruder, and the 250-micrometer sheet which consists of monolayers of polylactic acid was obtained.

[0053] The vertical extension of the sheet mentioned above was increased 1.5 times, and subsequently to [1.5 times], after carrying out horizontal extension, it heat-treated at 160 degrees C. The pass time of a part for /and 2m extension / heat treatment each zone of the flow rate of the film after extension was 30 seconds, respectively.

[0054] Since Tm of the polylactic acid system film layer used as an outer layer is 170 degrees C, What is contained in this invention which can form the inner layer lower 10 degrees C or more than Tm of a polylactic acid system film layer among the above-mentioned examples of the aliphatic series polyester used for a inner layer Bionolle 1010 (Tm=114 degree C), It is the plaque cel H-7 (Tm=60 degree C) and the film which used biotechnology pole D300G (Tm=162 degree C), and these were made into examples 1-3. What, on the other hand, used the multilayer film which used biotechnology pole D400G (Tm=153 degree C), and the film of the monolayer configuration of polylactic acid was made into the examples 1 and 2 of a comparison.

[0055] The evaluation result of a film is shown in Table 1. In addition, on conditions as shown below, the measured value shown in front Naka measured, and was computed.

[0056] (1) With deltaP Abbe refractometer, the refractive index (alpha, beta, gamma) of rectangular cross 3 shaft orientations was measured, and it computed by the degree type.

[0057]

deltaP = $\{(\gamma + \beta) / 2\} - \alpha$ ($\alpha < \beta < \gamma$)

gamma: The maximum refractive index beta in a film plane: Since it is the refractive index of the refractive-index alpha: film thickness direction of the film plane inboard which intersects perpendicularly with it and **P specifies a polylactic acid system polymer film in this invention, when ***** etc. extended and heat-treated behind a laminating, if needed, film layers other than a polylactic acid system film layer were removed, and it measured about the polylactic acid system film.

[0058] (2) thermal-analysis PerkinElmer make -- using DSC-7, from the thermogram when carrying out the temperature up of the film sample 10mg of a raw material pellet or a polylactic acid system film layer by part for programming-rate/of 10 degrees C based on JIS-K7122, glass-transition-temperature Tg, melting out temperature Tm, amount deltaHm of crystal heat of fusions, and amount deltaHc of heat of crystallization were calculated, and it computed, respectively.

[0059] (3) The heat-sealing on-the-strength film sample was started by making MD (flow direction of a film) into a longitudinal direction in the shape of [of 10mm width-of-face x 100mm die length] a strip of paper, and after setting these two strip-of-paper-like samples so that it may intersect perpendicularly with the heat sealer which has the heat-sealing bar of superposition and 10mm width of face, it heated from one side at predetermined temperature, and heat sealed for 15 seconds by the pressure of 1.178 kg/cm². When a laminated film was used at this time, it set so that easily-adhesive processing sides might become inside.

[0060] An Inn Tesco universal testing machine 205 mold machine is used for the above-mentioned sample, and it is JIS. The amount of jointing remained until it fractured by part for 100mm/in exfoliation rate based on K-6854, and T mold friction test was performed until it was set to 1mm. or it makes peak value of the obtained time amount-stress into heat-sealing reinforcement and a seal is not carried out at all for a simple understanding -- having -- even if -- the value showed [the thing of less than 50 g/cm] ** and the thing of 500 or more g/cm for x, and 50 or more g/cm the thing of less than 500 g/cm as O.

[0061]

[Table 1]

表 1

		実施例1	実施例2	実施例3	比較例1	比較例2
外 層	材 料	ビオノーレ 1010	ブラクセル H-7	バイオボール D400G	バイオボール D300G	ポリ乳酸 単層 L/D=98:2 Tm=170℃
	Tm (℃)	114	60	153	162	
内層と外層とのTm差 (℃)		56	110	17	8	
内酸ム 層系の ポフ特 リィ性 乳ル値	$\Delta P (\times 10^{-3})$	10.5	10.5	10.5	10.5	10.5
	$\Delta Hm - \Delta Hc (J/g)$	50	50	50	50	50
	$(\Delta Hm - \Delta Hc) / \Delta Hm$	0.95	0.95	0.95	0.95	0.95
ヒート シール 強度	ヒートシール温度 100℃	×	○	×	×	×
	ヒートシール温度 125℃	○	○	×	×	×
	ヒートシール温度 150℃	○	○	○	×	×
	ヒートシール温度 175℃	○	○	○	○	○
	ヒートシール温度 200℃	×	×	×	×	×
		(溶解)	(溶解)	(溶解)	(溶解)	(溶解)

It turns out that the heat-sealing engine performance suitable in a large temperature requirement for the examples 1-3 whose differences of T_m of a inner layer (base material) and the outermost layer are 10 degrees C or more is obtained so that more clearly than Table 1. On the other hand, the example 1 of a comparison whose difference of T_m is 10 degrees C or less, and the example 2 of a comparison which is a monolayer are inferior in the heat-sealing engine performance.

[0062] (Example 2 of an experiment) The biaxial extension heat setting polylactic acid film with a thickness of 40 micrometers obtained by the same approach as the example 2 of a comparison was used as the base (base material), and lamination and a two-layer laminated film were produced to the tubular blown film later mentioned to the one side of the base by the dry lamination method.

[0063] as the denaturation PVA system which is crystallinity -- the Nippon Synthetic Chemical Industry Co., Ltd. make -- Mater-Bi AF-05H ($T_m=136$ degree C) -- As a cellulose ester compound which is amorphism nature, the constituent of the acetic-acid cotton [by Daicel Chemical Industries, Ltd.] L-40, and dibutyl horse mackerel peat 43 section (with no T_m - $T_g=103$ degrees C), As a polylactic acid system polymer which is amorphism nature, L body / D object =86/14, the polymer of weight average molecular weight 200,000 (with no T_m - $T_g=55$ degrees C), Furthermore, the tubular blown film with a thickness of 10-15 micrometers was manufactured by BUR (blow-up ratio) 2.5-4.4 using 30mmphi monopodium extruder equipped with the facility for tubular blown films using the polylactic acid used for the base.

[0064] a biaxial extension heat setting polylactic acid system film top -- as adhesives -- the product made from Japanese Polyurethane Industry -- after applying to the thickness of 2-5 micrometers by the coating machine using the mixture of NIPPORAN 3022/coronate L=9/1, the three above-mentioned kinds of tubular blown films were stuck by pressure, it aged for 40 degree-Cx two days, adhesives were stiffened, and the multilayer biodegradability plastic film of examples 4-6 and the example 3 of a comparison was obtained.

[0065] The evaluation result of these laminated films is shown in Table 2.

[0066]

[Table 2]

表 2

		実施例 4	実施例 5	実施例 6	比較例 3
種 フイル 用ム	材 料	マタービー AF-05H	酢酸綿L-50 組成物	ポリ乳酸 L/D=86:14	ポリ乳酸 L/D=98:2
	T_m (°C)	136	なし	なし	170
	T_g (°C)	-28	103	58	58
ヒート シール 強度	ヒートシール温度 100°C	×	△	○	×
	ヒートシール温度 125°C	×	△	○	×
	ヒートシール温度 150°C	○	○	○	×
	ヒートシール温度 175°C	○	○	○	○
	ヒートシール温度 200°C	×	×	×	×
		(溶解)	(溶解)	(溶解)	(溶解)

It turns out that the heat-sealing engine performance with the example 1 whose difference of T_m of a polylactic acid system film and the biodegradability plastic film which is the outermost layer of one side is 10 degrees C or more and the examples 2 and 3 whose biodegradability plastic film which is the outermost layer of one side is amorphism nature suitable in a large temperature requirement is obtained so that more clearly than Table 2. On the other hand, the example 3 of a comparison without the difference of T_m is inferior in the heat-sealing engine performance.

[0067] (Example 3 of an experiment) Vertical extension was carried out on the conditions which show

the non-extended sheet of the multilayer biodegradability plastic film which is three layers which formed Bionolle 1010 in the outer layer used in the example 1 in Table 3, subsequently horizontal extension was carried out, it heat-treated further, and the sheet of examples 8-11 was obtained. In addition, an example 7 is a non-extended sheet.

[0068] When investigated about the heat-sealing engine performance by the approach same about the acquired examples 7-11 as the examples 1 and 2 of an experiment, it turned out that the suitable heat-sealing engine performance is obtained in a large temperature requirement. Furthermore, tension breaking strength and heat shrink nature are shown in Table 3. In addition, on conditions as shown below, the measured value shown in front Naka measured, and was computed.

[0069] (4) Tension breaking strength tensile strength was measured based on JIS-K7127 using the Oriental energy machine tensilon II mold machine. The direction where TD intersects perpendicularly to the flow of a film in MD is shown to the flow direction of a film.

[0070] (5) a part for a heat shrink [as opposed to / measure the dimension, after starting a heat shrink nature film sample to 100mmx100mm and being immersed in a 80-degree C warm water bus for 300 seconds, and / the original dimension] -- (%) was computed comparatively.

[0071]

[Table 3]

表 3

		実施例 7	実施例 8	実施例 9	実施例 10	実施例 11
縦 延 伸	温度 (℃)	未 延 伸 シ ー ト	70	70	70	70
	延伸倍率		1.5	2.5	2.5	2.5
横 延 伸	温度 (℃)		75	70	70	70
	延伸倍率		1.5	2.5	2.5	2.5
* ΔP ($\times 10^{-3}$)		0.1	3.4	10.5	10.5	10.5
熱 処 理 温 度 (℃)		—	80	40	100	160
* $\Delta H_m - \Delta H_c$ (J/g)		10	22	35	43	49
* $(\Delta H_m - \Delta H_c) / \Delta H_m$		0.17	0.43	0.69	0.83	0.94
引張り破断強度 (kg/cm ²)	MD	720	880	1320	1240	1290
	TD	700	850	1210	1170	1200
収 縮 率 (%)	MD	1	19	14	2	0
	TD	0	27	54	3	0

* ポリ乳酸系フィルムの測定値

Tensile strength is inadequate, although its contraction is small since an example 7 is a non-extended sheet. An example 8 has planar orientation degree ΔP in the range of 3×10^{-3} to 30×10^{-3} , and since it is extending, it is suitable as a heat shrink film which has moderate tensile strength. An example 9 has planar orientation degree ΔP in the above-mentioned range, and since the heat treatment temperature after extension is suitable, it is the heat shrink film excellent in tensile strength and heat shrink nature. On the other hand, ΔP is 0.75 or more and 3×10^{-3} to 30×10^{-3} and $(\Delta H_m - \Delta H_c)$ are [20 or more J/g and $\{(\Delta H_m - \Delta H_c) / \Delta H_m$ of examples 10 and 11}] the heat dimensional-stability films which were excellent in tensile strength and heat dimensional stability.

[0072] That is, the multilayer biodegradability plastic film which the multilayer biodegradability plastic film of this invention is excellent in heat-sealing nature with extension conditions, and has moderate tensile strength, and has heat shrink nature or heat dimensional stability can be obtained so that more clearly than Table 3.

[0073]

[Effect of the Invention] Since the multilayer biodegradability plastic film of this invention has the outstanding heat-sealing nature, can be used for a general packing material etc. and has biodegradability, it is environment-friendly.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The melting out temperature T_m of the biodegradability plastic film which has the film which consists of a constituent which makes a principal component a polylactic acid system polymer or this, and is multilayer biodegradability plastic film one [at least] outermost layer of whose is biodegradability plastic film, and forms said outermost layer is multilayer biodegradability plastic film characterized by being lower than the melting out temperature T_m of the film which consists of a constituent which makes a principal component said polylactic acid system polymer or this 10 degrees C or more.

[Claim 2] The biodegradability plastic film which it has the film which consists of a constituent which makes a principal component a polylactic acid system polymer or this, and it is multilayer biodegradability plastic film one [at least] outermost layer of whose is biodegradability plastic film, and the film which consists of a constituent which makes a principal component said polylactic acid system polymer or this has a melting out temperature T_m , and forms said outermost layer is multilayer biodegradability plastic film characterized by being an amorphous film.

[Claim 3] Multilayer biodegradability plastic film according to claim 1 or 2 characterized by the melting out temperature T_m of the film which consists of a constituent which makes a principal component said polylactic acid system polymer or this being 100 degrees C or more.

[Translation done.]